Porogen Residue Free Ultra Low-*k* PECVD Material: Fabrication, Optical and Mechanical Properties

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The ITRS roadmap scaling of ultra-large-scale integrated circuits requires mechanically robust materials with low *k*-value. Low-*k* materials currently used in Cu/low-*k* integration scheme have *k*-values between 2.7 and 3.0. One of the limiting factors in further reduction of *k*-value is mechanical robustness, since more than 32 % of porosity needs to be introduced to PECVD film to achieve the *k*-values below 2.3. In this work we report a new curing procedure of enhanced chemical vapor deposited (PECVD) low-*k* film. The new curing allows us to achieve a mechanically robust and hydrophobic ultra low-*k* film (k < 1.8). The method is based on subsequent treatment of deposited films in the afterglow of H_2-based plasma and UV assisted thermal curing. The porogen removal by hydrogen plasma afterglow with the following UV-curing allows us to produce, a porogen-residue-free ultra low-*k* films with porosity higher than 50% and high elastic modulus of ~ 5 GPa.

The porogen molecules, cyclic aromatic hydrocarbons, are introduced into a SiOCH film by co-deposition with the matrix material in a PECVD process. To achieve porous films the porogen is removed from the films using UV assisted thermal curing [1]. The porogen molecules are photo-dissociated by UV light with the formation of volatile hydrocarbons and nonvolatile carbon-rich residues (porogen residue). The effect of the porogen residue on optical, chemical and mechanical properties of CVD films has recently been reported [2,3]. Degradation of the mechanical properties as a result of porogen residue removal from advanced PECVD low-*k* films (*k*<2.3) during a photo mask ash has been recognized as an integration challenge [3]. Therefore, it is necessary to optimize the curing process of low-*k* films in order to avoid porogen residue formation. For this purpose, as deposited low-*k* films (with porogen) were exposed in He/H_2 downstream plasma (DSP) at 280 °C and then UV cured at 430 °C. Experiments were carried out with 60 nm, 120 nm and 190 nm thick PECVD films. The optical spectra and mass loss of low-*k* films (Figures 1 and 2) show that, the conventional thermo-assisted UV curing results in formation of porogen residues in contrast to He/H_2-DSP curing. The films were evaluated by ellipsometric porosimetry (EP) (pore size distribution and water absorption), FTIR (bonding structure), UV spectroscopic ellipsometry (optical properties). All these data will be discussed together with nano-indentation (NI) data showing significant improvement of mechanical properties in comparison with the conventional curing (Figure 3) [4]. Elastic modulus of ~5 GPa for porogen residue free low-*k* film with 50 % of open porosity and pore radius of 1.5 nm and *k*-value of 1.8 (as measured by Hg-probe) was obtained using two step H-based afterglow plasma and UV-curing approach.

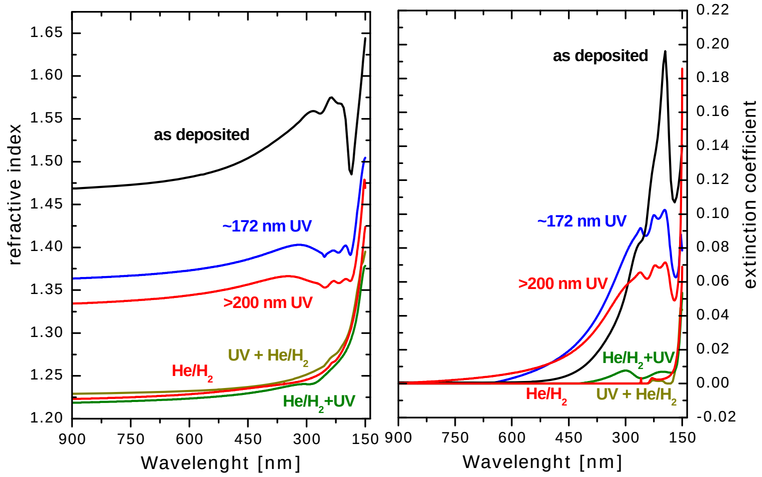

Fig. 1 Optical properties of low-*k* films as measured by UVSE: as deposited film (with porogen); as deposited low-*k* films cured with UV light wavelength of 172 nm and > 200 nm, He/H_2-DSP and two combined He/H_2-DSP and 172 nm UV cures. The extinction coefficient is proportional to organic residues content. The treatments involving He/H_2-DSP results in significant reduction of organic residues in comparison with standard UV-curing process using excimer (~172 nm) or broadband (> 200 nm) UV source.

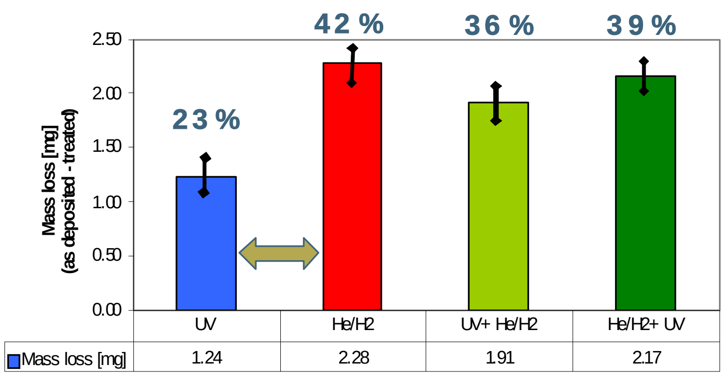

Fig. 2 The mass loss of He/H_2 and/or 172 nm UV treated films with thicknesses around 60 nm as measured by mass balance on 300 mm wafers. Error bars represent the mass measurement error due backside cleaning. The percentage number reflects approximated mass loss of the film after treatment. The conventional 172 nm UV curing process leaves approximately 46 % more mass of cross-linked porogen (porogen residue) in comparison to He/H_2-DSP treatment. The results correspond with UVSE data (see extinction coefficient).

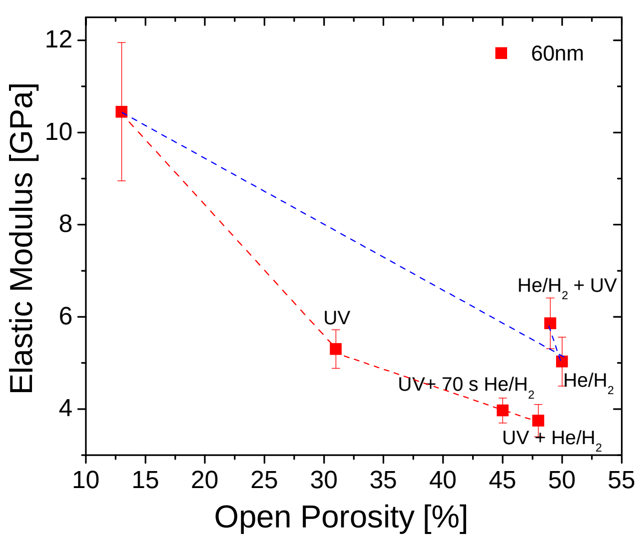

Fig. 3 Elastic modulus (EM) as measured by NI versus open porosity as measured by EP for as deposited and UV treated 60 nm films (relative study). The EM drop after all treatments due to porogen removal. When subsequent UV + He/H_2-DSP treatment is applied the EM is reduced due to porogen residues removal. The He/H_2-DSP plus UV-curing results in improved EM if to compare with conventional UV curing. The removed porogen residues do not prevent cross-linking of Si-O-Si matrix.

References

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